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双金属燃料电池催化剂的纳米结构设计与制备

Nanostructured Design and Synthesis of the Bimetallic Fuel Cell Catalysts

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摘 要

低温燃料电池以其清洁、高效、安全、可移动、操作条件温和等优点，被誉为是最具大规模产业化前景的一类燃料电池。低温燃料电池包括质子交换膜燃料电池、直接醇燃料电池和直接酸燃料电池等。但是这些燃料电池催化剂均使用价格昂贵、资源稀缺的贵金属铂作为主要活性组分，由此造成的燃料电池成本高昂已成为制约燃料电池商业化进程的重要因素。另外，铂作为燃料电池的催化剂还具有容易中毒的缺点。因此，针对燃料电池成本高，反应活性低和稳定性差等制约其商业化的主要因素，展开材料的合理设计，通过提高材料的物理和化学性质，寻找可行的新型催化剂材料路线显得尤为重要。本论文具体内容主要包括以下几个方面：

一、设计甲酸电催化氧化反应的高活性高稳定的催化剂要求调控 Pt 基催化剂表面上的 Pt 原子“三聚体”的数量。根据以上要求，本章通过自发置换反应来制备不同 Pt:Pd 比例的 Pt-Pd/C 催化剂，从而达到调控 Pt-Pd/C 催化剂表面 Pt 原子“三聚体”的目的。HS-LEIS 结果表明基底 Pd 纳米粒子的表面部分被 Pt 原子覆盖了，并且表面 Pd 基底和 Pt 原子存在相互作用。电化学测试结果显示 Pt-Pd/C(Pt:Pd=1:250)催化剂对于甲酸的电氧化活性和稳定性都高于 Pd/C 和商业 Pt/C，是因为表面不连续的 Pd 和 Pt 活性位点抑制了 CO 的生成。该催化剂的成本等同于等量的 Pd/C 的价格，从而降低了成本。

二、为了进一步优化燃料电池甲酸电氧化反应的催化剂性能且降低贵金属 Pt 的使用量。本章采用气氛 H_2 焙烧直接还原 PdFe 前驱体的方法，从而得到 Pd 基双金属 PdFe/C 催化剂。这种制备方法简易，适用于大规模生产，且生产成本低。电化学性能测试结果显示了 PdFe/C(Pd:Fe=2:1)催化剂的质量活性超过相同反应条件制备出的 Pd/C 催化剂 6 倍。PdFe/C(Pd:Fe=2:1)催化剂的高性能是 Pd 组分和 Fe 组分的相互作用的结果。

三、为解决目前甲酸电池中 Pd 催化剂活性不高、抗毒性不好的问题，尝试制备了一种以 Fe 为核，Pd 修饰 Fe 表面结构的 Pd-Fe/C 催化剂，所制得的催化剂 PdFe 活性组分颗粒粒径(约 3.7nm)较之纯 Pd 催化剂(约 3.8nm)差不多。该催化剂对于甲酸电氧化反应表现出了较高的催化活性，可达 Pd/C 催化剂的 11 倍，更为重要的是该催化剂对于甲酸的电氧化反应是通过直接机理进行的。结合催化剂

的表征结果，分析导致 Pd-Fe/C 催化剂高性能的原因有如下两点：一是 Fe 更倾向于被氧化和 Pd 的相对弱倾向于被氧化，从而影响催化剂表面 $Pd^{2+}/(Pd^{2+}+ Pd^{0})$ 比例。二是 Pd^{0} 是甲酸电催化氧化反应的主要活性位点。

四、 Pd-Fe/C 催化剂尺寸均一，组成可控为建立双金属组成与催化活性的关系提供了优质的材料基础。其中 Pd-Fe/C(Pd:Fe=1:5)催化剂的催化活性最优，并且考虑在提高活性和稳定性的前提下进一步降低催化剂成本问题。在此基础上，故选用上述的低 Pd 含量的 Pd-Fe/C(Pd:Fe=1:5~1:15)这三个催化剂进行氩气(Ar)气氛热处理。XRD 表征结果显示的是 Pd-Fe/C(Pd:Fe=1:5)和 Pd-Fe/C(Pd:Fe=1:10)催化剂焙烧后都出现了 PdO 氧化物并未发现 Pd 的衍射峰，而 Pd-Fe/C(Pd:Fe=1:15)催化剂焙烧后同时出现了 Pd 和 PdO 的衍射峰。电化学测试结果表明 Pd-Fe/C(Pd:Fe=1:5)和 Pd-Fe/C(Pd:Fe=1:10)催化剂焙烧后的甲酸电氧化的催化性能低于焙烧前的催化性能，而 Pd-Fe/C(Pd:Fe=1:15)焙烧后的催化性能却优于焙烧前催化剂的性能。透过这种现象揭示了本章是通过控制 PdFe 组分，调节两种金属颗粒比例，然后对不同组分的 Pd-Fe/C 催化剂进行焙烧，从而调控催化剂表面氧化物-金属的配比，最终用于甲酸电催化氧化反应。

关键词：

燃料电池；甲酸电氧化；置换反应；PtPd 催化剂；PdFe 催化剂

Abstract

Low temperature fuel cells (LTFC) have attracted much attention all over the world due to their abilities to deliver clean and high power density, safety, portability, convenience in operation and commercialization viability in the future. LTFCs are predicted to be the best candidate for industrialization applications. Low temperature fuel cells include proton exchange membrane fuel cells (PEMFCs), direct alcohol fuel cells (DAFCs) and direct acid fuel cells et al. Commercialization of these fuel cells is seriously hindered by the usage of expensive and scare Pt catalysts, which led to high cost. Besides the high cost, Pt catalysts for fuel cell applications are suffered from poisoning as well. Therefore, it is important to explore a feasible and novel fuel cell catalyst route by improving the chemical and physical properties of these materials against the drawbacks of commercialization due to high cost, sluggish kinetics and long-term stability of fuel cell catalysts. The main results can be summarized as follows:

Firstly, the design of active and durable catalysts for formic acid (FA) electrooxidation requires controlling the amount of three neighboring platinum atoms in the surface of Pt-based catalysts. Such requirement is studied by preparing Pt decorated Pd/C (donated as Pt-Pd/C) with various Pt:Pd molar ratios via galvanic displacement making the amount of three neighboring Pt atoms in the surface of Pt-Pd/C tunable. Cyclic voltammetry and chronoamperometric measurements, demonstrating that Pt-Pd/C (the optimal molar ratio, Pt:Pd=1:250) exhibits superior activity and durability than Pd/C and commercial Pt/C (J-M, 20%) catalysts for FA electrooxidation. The high-sensitivity low-energy ion scattering (HS-LEIS) studies that most of the Pd-based surfaces had already been covered partly by Pt atoms, and that an interaction occurred between the Pd substrate and the Pt in the surface. The controlled synthesis of Pt-Pd/C lead to the formation of largely discontinuous Pd and Pt sites and inhibition of CO formation, exhibiting unprecedented electrocatalytic performance toward FA electrooxidation while the cost of the catalyst almost the same as Pd/C.

Secondly, to optimize nanocatalyst performance and durability for formic acid oxidation reaction in fuel-cell applications and further reduce the cost of Pt, we look beyond Pd–based intermetallic nanoparticles and describe a simple method of preparing PdFe intermetallic nanoparticles on carbon by post-treatment of the asprepared PdFe precursors at high temperature under flowing H_2.The facile method described herein is suitable for large-scale, lower-cost production. The PdFe/C(Pd:Fe=2:1) nanocatalyst exhibited over 600% increase in mass activity when compared with the Pd nanoparticles under similar testing conditions. The electrocatalytic activity for formic acid oxidation has also been studied and improved by the interaction between Pd and Fe.

Thirdly, since Pd catalysts are suffered from low activity and poor poisoning resistance in formic acid oxidation, the Pd-Fe/C catalyst using Fe core is prepared to solve these issues. It was found that the particle size for Pd-Fe/C(Pd:Fe=1:5) (about 3.7nm) is almost the same as single Pd catalyst (about 3.8nm). A 11-fold formic acid oxidation activity enhancement was obtained on Pd-Fe/C(Pd:Fe=1:5) relative to Pd/C. Moreover, the formic acid oxidation on Pd-Fe/C followed the direct pathway. This finding can be associated with two important attributes, a higher propensity of Fe and the lower propensity of Pd to surface oxidation ($Pd^{2+}/(Pd^{2+}+ Pd^{0})$), as proven by the relatively high activity observed for the as-prepared Pd-Fe/C nanocatalyst. Moreover, the Pd^{0} active sites play an important role in formic acid oxidation.

Fourthly, based on the understanding of the relationship between the composition and activity and considering to raise the activity and stability of Pd-Fe/C catalysts and reduce the catalyst cost, this section studied Pd-Fe/C catalysts by post-treatment of the as-prepared Pd-Fe/C(Pd:Fe=1:5~1:15) catalysts at certain temperature under flowing Ar. XRD results found the existence of PdO diffraction peaks for Pd-Fe/C(Pd:Fe=1:5) Pd-Fe/C(Pd:Fe=1:10) and catalyst, Pd and PdO diffraction peaks for Pd-Fe/C(Pd:Fe=1:15) catalyst. Chronoamperometric measurements demonstrated that the activity of Pd-Fe/C(Pd:Fe=1:5) and Pd-Fe/C(Pd:Fe=1:10) after heat-treatment catalysts is worse than before-treatment catalysts, however, the activity of Pd-Fe/C(Pd:Fe=1:15) after heat-treatment catalyst is superior to Pd-Fe/C(Pd:Fe=1:15)

catalyst. From this phenomenon, this section stuied controlling the composition through controlling the component ratio, and then heat-treatment of as-prepared aboved Pd-Fe/C catalysts for adjusting the oxide - metal ratio towards formic acid oxidation.

Keywords:

Fuel Cell; Formic Acid Oxidation; Displacement Reaction; PtPd catalyst; PdFe catalyst